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(54) ESTERIFIED STARCH COMPOSITION

ZUSAMMENSETZUNG VERESTERTER STÄRKE

COMPOSITION D'AMIDON ESTERIFIÉ

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(56) References cited:
WO-A-92/19675 GB-A- 964 799

- INDUSTRIAL AND ENGINEERING CHEMISTRY
vol. 49, no. 8, 1 August 1957, pages 1247 - 1248
IVAN A. WOLFF ET AL. 'MIXED ESTERS OF
AMYLOSE'

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Description

The present invention relates to degradable polymer compositions capable of being formed by heat and pressure into articles having good dimensional stability and physical properties.

It is known that starch may be heated under pressure to form a melt suitable for the production of shaped articles. Such starch-based shaped articles may exhibit the disadvantages of relatively poor physical properties under high relative humidity conditions and a relatively high tendency to embrittlement under relatively low humidity conditions.

Attempts to overcome these problems by the replacement of the above mentioned starch by maize starch esters having a low degree of substitution, as commonly found in the starch industry, have generally been unsuccessful, often resulting in weak, brittle, hydrophilic materials having a poor balance of physical properties. It is an object of the present invention to overcome, at least in part, the above mentioned disadvantages.

GB-A-964799 discloses a composition which flows under heat and pressure and which is water soluble comprising a derivative of an amylaceous material, a plasticizer for the derivative and water, said derivative being an ether, ester, mixed ether, mixed ester, mixed ether-ester, or a mixture of two or more thereof. It is reported that the MS (moles of etherifying agent per anhydroglucose unit) of the alkyl or acetyl derivatives should not exceed an MS of 1.5; at MS of 2 there were water insoluble. Acetyls having MS of 0.3 to 1.5 are disclosed.

Industrial and Engineering Chemistry, Vol. 49 No. 8, 1957, pages 1247-1248 describes mixed aliphatic esters of amylose which can be converted to films and moulded products. This reference strictly deals with amylose triesters.

WO 92/19675 concerns moisture-proof, thermoplastic, environmentally friendly, thermoplastically produced products and cast films of processable starch materials consisting of starchy fat acyl compounds obtainable from amylose-rich starches and softeners. WO 92/19675 is prior art only according to Art. 54 (3) EPC. The reference discloses starch acetates and in one aspect suggests to replace part of the acetic acid by long chain acids.

According to the present invention there is provided a composition as obtained from a melt comprising esterified starch, plasticizer and optionally further additives which is characterized in that the esterified starch has a degree of substitution of from 1.8 to 2.9, the esterified starch comprising at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, hexanoate, heptanoate and octanoate, except starch esters having both an acetate and C₆ carboxylic acid residue, and wherein the plasticizer has the formula



wherein A is a saturated or unsaturated aliphatic or alicyclic residue; n is an integer; m is an integer of zero to 6, whereby the sum m + n is an integer from 1 to 6, and R and R₁ are independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having 1 to 20 carbon atoms, or



wherein A is a saturated or unsaturated aliphatic or alicyclic residue; x is an integer of 1 to 2; y is an integer from zero to 4; z is an integer from zero to 4; whereby the sum of y + z is an integer of 2 to 4 and R and R₁ are independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having 1 to 6 carbon atoms,

or is selected from the group consisting of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, di-2-ethylhexyl phthalate, di-n-octyl phthalate, di-isooctyl phthalate, di-isononyl phthalate, di-isodecyl phthalate, dicyclohexylphthalate, dimethylcyclohexyl phthalate, dimethylglcol phthalate, trichloroethyl phosphate, cresyl di phenyl phosphate, triphenyl phosphate, tri-cresyl phosphate, butyl phthalylbutyl glycolate, tributyl phosphate, N-ethyl-o,p-toluenesulfonamide, diethyleneglycole dibenzoate, dipropylene glycol dibenzoate and mixtures thereof.

The starch ester is a mixed ester, i.e. having different kinds of ester groups attached to the same molecule, as are obtained for example by reaction of starch with a mixed acid anhydride or a mixture of different acid anhydrides. Such a mixed acid anhydride may be for example an acid anhydride made from acetic acid and propionic acid; a mixture of different acid anhydrides may be for example a mixture of acetic acid anhydride and propionic acid anhydride.

The esterified starch as used in this invention may be made from a starch as obtained from potatoes, rice, tapioca, corn, pea, rye, oats, and wheat with the respective known amylose content. However, the amylose content of the starch is preferably at least about 50% by weight with respect to that of the starch.

The composition may further include one or more members selected from the group consisting of extenders; fillers; wood derived materials; oxides of magnesium, aluminum, silicon, and titanium; lubricants; mold release agents; plasticisers; stabilisers; colouring agents; flame retardants; boron-containing compounds; alkali and alkaline earth metal salts; thermal stabilisers; and melt flow accelerators; and mixtures thereof.

The invention further provides the composition according to this invention when shaped into articles, for example bottles, strands, sheets, films, packaging materials, pipes, cups, rods, laminated films, sacks, bags, pharmaceutical capsules, foams, granulates and powders by a process including injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, extrusion moulding, co-extrusion, foaming, profile extrusion and combinations thereof.

The invention still further provides the composition of the present invention in the form of a melt.

The present invention will be further apparent from the following description taken in conjunction with the accompanying examples, and appended claims.

The starch ester is a mixed ester comprising at least two different types of alkylcarbonyl groups (i.e. of different lengths) in the same molecule and as such may be of the kind as obtained by reaction of starch with a mixed anhydride or with a mixture of different acid anhydrides.

It is preferred that such mixed starch esters comprise at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, and hexanoate, residues bound to the same molecule.

Particularly preferred starch diesters comprise both acetate and propionate groups or both acetate and butyrate groups or both propionate and butyrate groups or both pentanoate and butyrate groups bound to the same molecule.

In the case of starch diesters, the ratio of the types of ester groups comprised by the starch ester may vary greatly, but preferably is in the range of about 1:1 to about 1:20.

The degree of the total substitution of the esterified starch is from 1.8 to 2.9, independent of the type of substitution. The preferred degree of substitution is from about 1.8 to about 2.5.

Examples of starch esters are given in Table 1, for illustrative purposes.

Table 1

Example No.	starch type	ester type	degree of substitution
1.	corn	acetate	1.75
2.	corn	acetate	2.58
3.	corn	propionate	1.84
4.	corn	propionate	2.47
5.	Hylon VII*	acetate	1.83
6.	Hylon VII*	acetate	2.34
7.	Hylon VII*	acetate	2.81
8.	Hylon VII*	propionate	1.89
9.	Hylon VII	propionate	2.55

* Hylon VII is a high amylose corn starch with an amylose content of about 70%, sold by National Starch and Chemical Co, USA.

Examples of mixed starch esters are given in Table 2.

Table 2

Ex.Nr.	starch type	amylose content	ester type (1)	ester type (2)	ratio ester 1 : ester 2	total DS*
10.	corn	27%	acetate	pro'ate	25:75	2.36
11.	corn	27%	acetate	pro'ate	50:50	1.85
12, for illustrative purpose	corn	27%	acetate	pro'ate	75:25	1.60
13.	corn	27%	acetate	but'ate	05:95	1.82
14.	corn	27%	acetate	but'ate	40:60	2.05
15.	corn	27%	acetate	but'ate	95:05	2.59

* = degree of substitution

Table 2 (continued)

Ex.Nr.	starch type	amylose content	ester type (1)	ester type (2)	ratio ester 1 : ester 2	total DS*
16.	corn**	70%	acetate	pro'ate	25:75	2.06
17.	corn**	70%	acetate	pro'ate	50:50	1.84
18.	corn**	70%	acetate	pro'ate	75:25	1.77
19.	corn**	70%	acetate	but'ate	05:95	1.87
20.	corn**	70%	acetate	but'ate	40:60	2.06
21.	corn**	70%	acetate	but'ate	95:05	2.73

* = degree of substitution

corn** = Hylon VII

pro'ate = propionate

but'ate = butyrate

Within the scope of this invention, any type of commercially available starch to produce the esterified starch may be used such as native starch selected from potatoes, rice, tapioca, corn, pea, rye, oats, maize, barley and wheat. However it is preferred that the amylose content of the starch is at least about 50% and preferably is higher than this, typically being in the range of about 70% by weight with respect to that of the starch.

A highly suitable starch is the high amylose genetically modified corn starch, Hylon VII, having an amylose content of about 75%, available from National Starch and Chemical Company of Funderne Avenue, Bridgewater, New Jersey NJ 08807, USA.

Whilst the substituted high amylose starches present in the inventive compositions are thermoplastic per se, ie in the absence of an added plasticiser, the composition further comprises a plasticiser by which the melting temperature of the esterified starch is reduced and the processability thereof improved.

Preferably, the plasticiser is present in an amount of from 5 to 60% by weight with respect to that of the starch.

The plasticiser may have a molecular weight of less than 2,000, and it is preferred that the molecular weight is between about 100 and about 1,000.

As a first alternative, the plasticisers may be summarized by the formula:

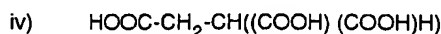
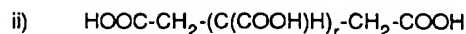
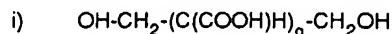


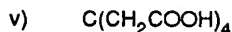
wherein: A is a saturated or unsaturated aliphatic or alicyclic residue; n is an integer from zero to 8; m is an integer from zero to 6; whereby the sum of m + n is an integer from 1 to 6, and R and R₁ are, independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having from 1 to 20 carbon atoms.

In one embodiment of compound (I), A is a saturated aliphatic residue having 2 to 8 carbon atoms; m is an integer from zero to 4; n is 0, 1, 2 or 3; the sum of m + n is 2 to 4; and R₁ and R₁ are independent of each other and are alkyl residues having from 1 - 6 carbon atoms.

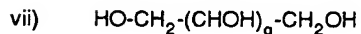
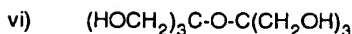
In a more preferred embodiment of compound (I), A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; m is an integer from zero to 4; n is 0, 1 or 2; the sum of m + n is 2 to 4; and R and R₁ are independent of each other are alkyl residues having 1, 2, 3 or 4 carbon atoms.

Compound (I) may be an ester derivative of at least one of the following members:





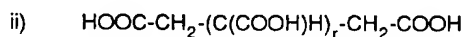
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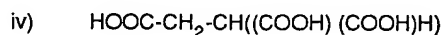
10 wherein: q and r are independently of each other 1, 2, 3 or 4 and R_2 is methyl or propyl.

Compound (I) may be a methyl, ethyl, propyl, or butyl carboxylate ester of a member selected from the group consisting of:

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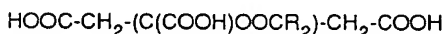
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where R_2 is methyl or propyl.

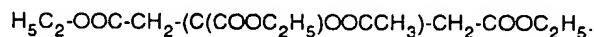
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In one embodiment of compound (I) it is preferred that the carboxylate ester is a tri-ethyl or tri-butyl carboxylate ester of:



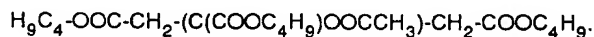
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where R_2 is methyl or propyl, and it is most preferred that compound (I) is selected from the group consisting of



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and



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Such most preferred compounds are known, and are, for example, sold under the Tradename of Citroflex A-2 plasticisers by Pfizer AG of Fluelastrasse 7, Postfach 2, 8048 Zuerich, Switzerland.

Another embodiment of compound (I) takes the form of a mono, di or tri ester of:

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viz the mono-, di-, or tri- acetate of glycerol.

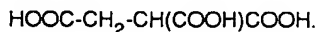
It is most particularly preferred that compound (I) is the tri-acetate of glycerol, viz:

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Compound (I) may also be a diacetate-monopropionate or dipropionate-monoacetate of glycerol or the diacetate or dipropionate of $OH-CH_2-C(COOH)H-CH_2OH$, or it may be selected from the trimethyl ester and tripropyl ester of:

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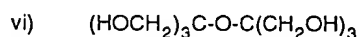
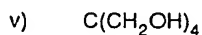
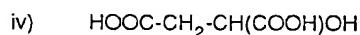
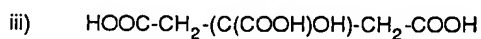
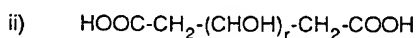
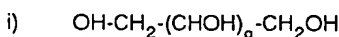
In a further alternative, the plasticiser has the general formula:



wherein A is a saturated aliphatic residue having 2 to 8 carbon atoms; x is one or two; y is an integer from zero to 4; z is an integer from zero to 4; the sum of y + z is 2 to 4; and R and R₁ are independent of each other and are alkyl residues having from 1 - 6 carbon atoms.

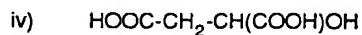
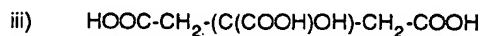
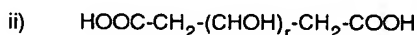
In a more preferred embodiment of compound (II), A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; x is one or two; y is an integer from zero to 4; z is an integer from zero to 4; the sum of y + z is 2 to 4; and R and R₁ are independent of each other and are alkyl residues having 1, 2, 3 or 4 carbon atoms.

Compound (II) may be an ester derivative of at least one of the following members:



wherein: q and r are independently of each other 1, 2, 3 or 4.

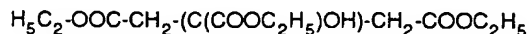
It is preferred that compound (II) is a methyl, ethyl, propyl or butyl carboxylate ester of a member selected from the group consisting of:



It is more preferred that the carboxylate ester is an ethyl or butyl ester, and it is most preferred that the compound is a tri-ethyl or tri-butyl carboxylate ester of:



Accordingly, the most preferred compounds of formula (II) have the formulae:

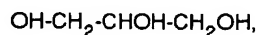


or

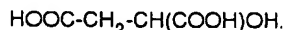


Such most preferred compounds are known, and are, for example, sold under the Tradename of Citroflex plasticisers by Pfizer AG of Fluelastrasse 7, Postfach 2, 8048 Zuerich, Switzerland.

Other forms of compound (II) for use according to the present invention include the diacetate and dipropionate of:



and the monoacetate-dimethyl ester and mono-acetate-dipropyl ester or mono-propionate-dipropyl ester of:



The plasticiser, whether of formula (I) or (II) is present in the composition in an amount of from about 3% to about 60% by weight based on the weight of the composition. It is more preferred that the concentration of such plasticiser is from about 5% to about 30%, and most preferred that the said concentration is from about 8% to about 18% by weight based on the weight of the composition.

Other suitable plasticisers include dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, di-2-ethylhexyl phthalate, di-n-octyl phthalate, di-isooctyl phthalate, di-isonyl phthalate, di-isodecyl phthalate, dicyclohexylphthalate, dimethylcyclohexyl phthalate, dimethylglycol phthalate, trichloroethyl phosphate, cresyl di phenyl phosphate, triphenyl phosphate, tri-cresyl phosphate, triacetyl citrate, triethyl acetyl citrate, triethylene glycol di (2-ethylbutyrate), diacetin, butyl phthalylbutyl glycolate, acetylated monoglycerides, triethyl citrate, diethyl succinate, dimethyl sebacate, tributyl phosphate, di-n-hexyl azelate, di-isooctyl azelate, di-(2-ethylhexyl), azelate, dicapryl adipate, N-ethyl-o,p-toluenesulfonamide, diethyleneglycoledibenzoate, dipropylene glycol dibenzoate and mixtures thereof.

Particularly suitable plasticisers are glycerol triacetate, dimethyl sebacate, diethyl succinate, acetyl triethyl citrate, or mixtures thereof, which may be present in the composition in an amount of from about 5 to about 45% by weight with respect to that of the starch ester.

The composition may further contain extenders; fillers; wood derived materials; oxides of magnesium, aluminum, silicon, and titanium; lubricants; mold release agents; plasticisers; stabilisers; colouring agents; flame retardants; boron-containing compounds; alkali and alkaline earth metal salts; thermal stabilisers; and melt flow accelerators; and mixtures thereof.

The preferred thermal stabiliser and mold release agent are respectively butylated hydroxy toluene and stearyl stearamide which may be present in the composition in amounts respectively of from about 0.01 to about 5% and from about 0.01 to about 2%, by weight with respect to the starch ester component of the composition.

In one embodiment of the invention, the composition further comprises a native or chemically modified (non esterified) starch selected from potatoes, rice, tapioca, corn, pea, rye, oats, and wheat.

The invention will be further apparent from the following Examples which are appended for illustration only and do not belong to the invention.

Example 1

The following formulation is prepared:

1000 grams of Hylon VII starch acetate having a degree of substitution of 2.0; 300 grams of glycerol triacetate; 5 grams of butylated hydroxy toluene and 3 grams of Stearyl Stearamide.

The mixture is thoroughly blended in an intensive mixer of the Henschel variety such as is known to the skilled man. Following blending, the mixture is allowed to rest for at least 24 hours.

The thus blended mixture is then extruded on a Berstorff twin screw extruder on which a stock temperature of 160°C (320 F) is maintained. The extrudate is then cooled and pelletised.

The thus cooled pellets are then placed in the hopper of a 170 CMD. Arburg injection moulding machine. The temperature zones are set as follows:

Zone 1: 127°C (260 F)

Zone 2: 154°C (310 F)

Zone 3: 154°C (310 F)

and tensile test pieces are produced at an injection molding pressure of about 550 bar. The thus produced test pieces

are translucent and exhibit excellent flexibility and toughness.

Example 2

The above Example is repeated except that the formulation contains the thermal stabiliser (butylated hydroxy toluene) at a concentration of between 0.05 and 2.0% by weight based on the weight of the starch ester. Similar tensile test pieces likewise having improved properties are produced.

Example 3

Example 2 is repeated except that the amount of plasticiser (glycerol triacetate) is varied from 5 to 45% by weight with respect to that of the starch ester in the composition. Similar tensile test pieces likewise having improved properties are produced.

Example 4

Example 2 is repeated except that the mold release agent (stearyl stearamide) concentration is increased to 1% by weight with respect to that of the total composition.

Example 5

Examples 1 to 4 are repeated except that the degree of substitution of the starch acetate is varied from 1.5 to 2.9. Similar tensile test pieces likewise having improved properties are produced.

The above Examples demonstrate the extrusion and injection mouldability of the present inventive compositions, which may be shaped into articles such as bottles, strands, sheets, films, packaging materials, pipes, cups, rods, laminated films, sacks, bags, pharmaceutical capsules, foams, granulates and powders by processes which include injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, extrusion moulding, co-extrusion, foaming, profile extrusion and combinations thereof.

Claims

1. A composition as obtained from a melt comprising esterified starch, plasticizer and optionally further additives, characterized in that the esterified starch has a degree of substitution of from 1.8 to 2.9, the esterified starch comprising at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, hexanoate, heptanoate and octanoate, except starch esters having both an acetate and C₆ carboxylic acid residue, and wherein the plasticizer has the formula

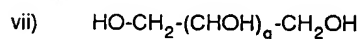
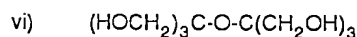
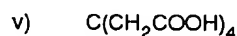
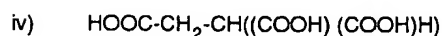
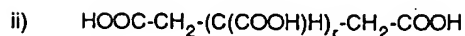
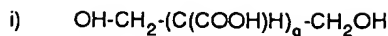


wherein A is a saturated or unsaturated aliphatic or alicyclic residue; n is an integer; m is an integer of zero to 6, whereby the sum m + n is an integer from 1 to 6, and R and R₁ are independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having 1 to 20 carbon atoms, or



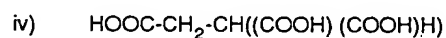
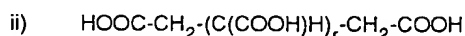
wherein A is a saturated or unsaturated aliphatic or alicyclic residue; x is an integer of 1 to 2; y is an integer from zero to 4; z is an integer from zero to 4; whereby the sum of y + z is an integer of 2 to 4 and R and R₁ are independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having 1 to 6 carbon atoms, or is selected from the group consisting of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, di-2-ethylhexyl phthalate, di-n-octyl phthalate, di-isooctyl phthalate, di-isononyl phthalate, di-isodecyl phthalate, dicyclohexylphthalate, dimethylcyclohexyl phthalate, dimethylglycol phthalate, trichloroethyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tri-cresyl phosphate, butyl phthalylbutyl glycolate, tributyl phosphate, N-ethyl-o,p-toluenesulfonamide, diethyleneglycol dibenzoate, dipropylene glycol dibenzoate and mixtures thereof.

2. A composition according to claim 1, in which the esterified starch comprises at least two members selected from the group consisting of acetates, propionates, butyrates, pentanoates, and hexanoates.
- 5 3. A composition according to any preceding claim, in which the starch ester has been obtained by reaction of starch with a mixed acid anhydride or with a mixture of different acid anhydrides.
4. A composition according to claim 2, in which the starch ester comprises both acetate and propionate groups bound to a common starch molecule.
- 10 5. A composition according to claim 2, in which the starch comprises both acetate and butyrate groups bound to a common starch molecule.
6. A composition according to claim 2, in which the starch comprises both propionate and butyrate groups bound to a common starch molecule.
- 15 7. A composition according to claim 2, in which the starch comprises both pentanoate and butyrate groups bound to a common starch molecule.
8. A composition according to any preceding claim, in which the ratio of the members is from about 20:1 to 1:20.
- 20 9. A composition according to claim 8, in which the ratio of the members is from about 3:1 to 1:3.
10. A composition according to claim 9, in which the ratio of the members is from about 2:1 to 1:2.
- 25 11. A composition according to claim 10, in which the ratio of the members is about 1:1.
12. A composition according to any preceding claim, in which the degree of substitution is from 1.8 to about 2.5.
- 30 13. A composition according to any preceding claim, in which the amylose content is at least about 50% by weight with respect to that of the starch.
14. A composition according to any preceding claim, in which the amylose content is at least about 70% by weight with respect to that of the starch.
- 35 15. A composition according to any preceding claim, in which the amylose content is at least about 80% by weight with respect to that of the starch.
- 40 16. A composition according to any preceding claim, in which the amylose content is at least about 90% by weight with respect to that of the starch.
- 45 17. A composition according to any preceding claim, which further includes a member selected from the group consisting of extenders; fillers; wood derived materials; oxides of magnesium, aluminum, silicon, and titanium; lubricants; mold release agents; plasticisers; stabilisers; colouring agents; flame retardants; boron-containing compounds; alkali and alkaline earth metal salts; thermal stabilisers; and melt flow accelerators; and mixtures thereof.
- 50 18. A composition according to any preceding claim, in which a plasticiser is present in an amount of from 5 to 60% by weight with respect to that of the starch ester.
19. A composition according to any preceding claim, wherein A is a saturated aliphatic residue having 2 to 8 carbon atoms; m is an integer from zero to 4; n is 0, 1, 2 or 3; the sum of m + n is 2 to 4; and R₁ and R₂ are independent of each other and are alkyl residues having from 1 - 6 carbon atoms.
- 55 20. A composition according to claim 19 in which A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; m is an integer from zero to 4; n is 0, 1, or 2; the sum of m + n is 2 to 4; and R₁ and R₂ are independent of each other and are alkyl residues having 1, 2, 3 or 4 carbon atoms.
21. A composition according to any one of claims 1 to 18, in which the plasticiser is an ester derivative of at least one of the following members:



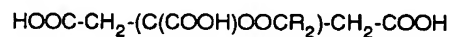
wherein: q and r are independently of each other 1, 2, 3 or 4 and R_2 is methyl or propyl.

22. A composition according to the preceding claim, in which the plasticiser is a methyl, ethyl, propyl, or butyl carboxylate ester of a member selected from the group consisting of:



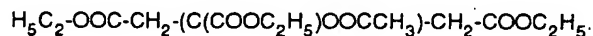
where R_2 is methyl or propyl.

23. A composition according to the preceding claim, in which the plasticiser is a tri-ethyl or tri-butyl carboxylate ester of:

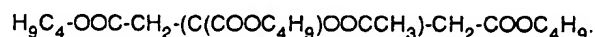


where R_2 is methyl or propyl.

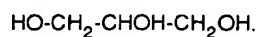
24. A composition according to the preceding claim, in which the plasticiser is selected from the group consisting of



and



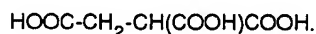
25. A composition according to any one of claims 1 to 18, in which the plasticiser is a mono, di or tri ester of:



26. A composition according to claim 25, in which the plasticiser is the tri-acetate of glycerol, viz:

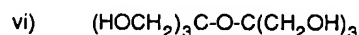
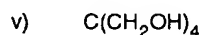
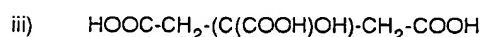
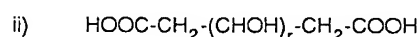
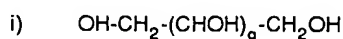


27. A composition according to any one of claims 1 to 18, in which the plasticiser is a diacetate-monopropionate or dipropionate-monoacetate of glycerol or the diacetate or dipropionate of $\text{OH-CH}_2\text{-C(COOH)H-CH}_2\text{OH}$, or the tri-methyl ester or tripropyl ester of:



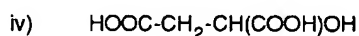
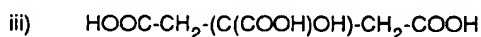
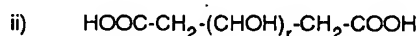
28. A composition according to any one of claims 1 to 18, in which A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; x is one or two; y is an integer from zero to 4; z is an integer from zero to 4; the sum of y + z is 2 to 4; and R and R₁ are independent of each other are alkyl residues having 1, 2, 3 or 4 carbon atoms.

29. A composition according to any one of claims 1 to 18, in which the plasticiser is an ester derivative of at least one of the following members:



wherein: q and r are independently of each other 1, 2, 3 or 4.

30. A composition according to the preceding claim, wherein the plasticiser is a methyl, ethyl, propyl or butyl carboxylate ester of a member selected from the group consisting of:



31. A composition according to the preceding claim, wherein the plasticiser is a tri-ethyl or tri-butyl carboxylate ester of :



32. A composition according to claim 31, wherein the plastiiser has the formula:



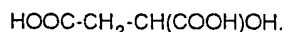
33. A composition according to claim 23, wherein the plasticiser has the formula :



34. A composition according to any one of claims 1 to 18, in which the plasticiser is the diacetate or dipropionate of:



or the monoacetate-dimethyl ester or mono-acetate-dipropyl ester or mono-propionate-dipropyl ester of:



35. A composition according to claim 18, wherein the plasticiser is selected from the group consisting of triacetyl citrate, triethyl acetyl citrate, triethylene glycol di (2-ethylbutyrate), diacetin, acetylated monoglycerides, triethyl citrate, diethyl succinate, dimethyl sebacate, di-n-hexyl azelate, di-isooctyl azelate, di-(2-ethylhexyl) azelate, dicapryl adipate, and mixtures thereof.

36. A composition according to claim 35, in which the plasticiser is dimethyl sebacate, diethyl succinate, acetyl triethyl citrate, or mixtures thereof.

37. A composition according to either of claims 34, 35 or 36, in which the thermal stabiliser and mold release agent are present in the composition in amounts respectively of from about 0.01 to about 5% and from about 0.01 to about 2%, by weight with respect to the starch ester component of the composition.

38. A composition according to any preceding claim, further comprising a native or chemically modified (non esterified) starch selected from potatoes, rice, tapioca, corn, pea, rye, oats, and wheat.

39. The composition of any one of claims 1 to 38, when shaped into articles.

40. Articles, according to claim 39, selected from the group consisting of bottles, strands, sheets, films, packaging materials, pipes, cups, rods, laminated films, sacks, bags, pharmaceutical capsules, foams, granulates and powders.

41. A process for making the articles of claim 40, selected from the group consisting of injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, extrusion moulding, co-extrusion, foaming, profile extrusion and combinations thereof.

42. The melt from which the composition of any one of claims 1 to 41 is obtained.

Patentansprüche

1. Zusammensetzung, erhalten aus einer Schmelze, die veresterte Stärke, Weichmacher und wahlweise weitere Zusätze umfaßt, dadurch gekennzeichnet, daß die veresterte Stärke einen Substitutionsgrad von 1,8 bis 2,9 aufweist und mindestens zwei Bestandteile aus der aus Acetat, Propionat, Butyrat, Pentanoat, Hexanoat, Heptanoat und Octanoat bestehenden Gruppe umfaßt, ausgenommen Stärkeester, die sowohl einen Acetat- als auch C₆-Carbonsäurerest aufweisen, und worin der Weichmacher die Formel



in der A ein gesättigter oder ungesättigter aliphatischer oder alicyclischer Rest, n eine ganze Zahl und m eine ganze Zahl von 0 bis 6 ist, wobei die Summe $m + n$ eine ganze Zahl von 1 bis 6 ist, und R und R_1 , unabhängig voneinander, ein gesättigter oder ungesättigter aliphatischer oder alicyclischer Rest mit 1 bis 20 Kohlenstoffatomen sind, oder die Formel



besitzt, in der A ein gesättigter oder ungesättigter aliphatischer oder alicyclischer Rest, x eine ganze Zahl von 1 bis 2, y eine ganze Zahl von 0 bis 4 und z eine ganze Zahl von 0 bis 4 ist, wobei die Summe $y + z$ eine ganze Zahl von 2 bis 4 ist, und R und R_1 , unabhängig voneinander, ein gesättigter oder ungesättigter aliphatischer oder alicyclischer Rest mit 1 bis 6 Kohlenstoffatomen sind,

oder aus der aus Dimethylphthalat, Diethylphthalat, Dibutylphthalat, Dihexylphthalat, Di-2-ethylhexylphthalat, Di-n-octylphthalat, Diisooctylphthalat, Diisononylphthalat, Diisodecylphthalat, Dicyclohexylphthalat, Dimethylcyclohexylphthalat, Dimethylglycolphthalat, Trichlorethylphosphat, Cresyldiphenylphosphat, Triphenylphosphat, Tricresylphosphat, Butylphthalylbutylglycolat, Tributylphosphat, N-Ethyl-o,p-toluolsulfonamid, Diethylenglycoldibenzoat, Di-propylenglycoldibenzoat und Mischungen daraus bestehenden Gruppe ausgewählt ist.

2. Zusammensetzung nach Anspruch 1, in welcher die veresterte Stärke mindestens zwei Bestandteile aus der aus Acetaten, Propionaten, Butyraten, Pentanoaten und Hexanoaten bestehenden Gruppe umfaßt.

3. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher der Stärkeester durch Umsetzen einer Stärke mit einem gemischten Säureanhydrid oder mit einer Mischung von verschiedenen Säureanhydriden erhalten worden ist.

4. Zusammensetzung nach Anspruch 2, in welcher der Stärkeester sowohl Acetat- als auch Propionatreste, die an ein gemeinsames Stärkemolekül gebunden sind, umfaßt.

5. Zusammensetzung nach Anspruch 2, in welcher die Stärke sowohl Acetat- als auch Butyratreste, die an ein gemeinsames Stärkemolekül gebunden sind, umfaßt.

6. Zusammensetzung nach Anspruch 2, in welcher die Stärke sowohl Propionat- als auch Butyratreste, die an ein gemeinsames Stärkemolekül gebunden sind, umfaßt.

7. Zusammensetzung nach Anspruch 2, in welcher die Stärke sowohl Pentanoat- als auch Butyratreste, die an ein gemeinsames Stärkemolekül gebunden sind, umfaßt.

8. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher das Verhältnis der Bestandteile etwa 20:1 bis 1:20 ist.

9. Zusammensetzung nach Anspruch 8, in welcher das Verhältnis der Bestandteile etwa 3:1 bis 1:3 ist.

10. Zusammensetzung nach Anspruch 9, in welcher das Verhältnis der Bestandteile etwa 2:1 bis 1:2 ist.

11. Zusammensetzung nach Anspruch 10, in welcher das Verhältnis der Bestandteile etwa 1:1 ist.

12. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher der Substitutionsgrad 1,8 bis etwa 2,5 beträgt.

13. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher der Amylosegehalt mindestens etwa 50 Gew.-%, bezogen auf die Stärke, beträgt.

14. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher der Amylosegehalt mindestens etwa 70 Gew.-%, bezogen auf die Stärke, beträgt.

15. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher der Amylosegehalt mindestens etwa 80 Gew.-%, bezogen auf die Stärke, beträgt.

16. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher der Amylosegehalt mindestens etwa 90 Gew.-%, bezogen auf die Stärke, beträgt.

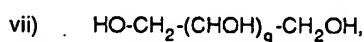
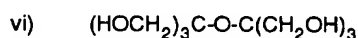
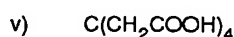
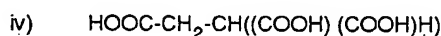
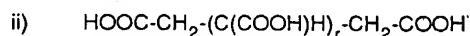
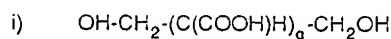
17. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, die darüberhinaus einen Bestandteil, ausgewählt aus der aus Verdünnungsmitteln, Füllstoffen, aus Holz erhaltenen Materialien, Oxiden von Magnesium, Aluminium, Silicium und Titan, Gleitmitteln, Formtrennmitteln, Weichmachern, Stabilisatoren, Farbmitteln, Antiflammitteln, borhaltigen Verbindungen, Alkali- und Erdalkalimetallsalzen, thermischen Stabilisatoren und Schmelzflußbeschleunigern und Mischungen daraus bestehenden Gruppe einschließt.

18. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, in welcher ein Weichmacher in einer Menge von 5 bis 60 Gew.-%, bezogen auf den Stärkeester, vorliegt.

19. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, worin A ein gesättigter aliphatischer Rest mit 2 bis 8 Kohlenstoffatomen, m eine ganze Zahl von 0 bis 4, n 0, 1, 2 oder 3 und die Summe m + n 2 bis 4 ist, und R und R₁, unabhängig voneinander, Alkylreste mit 1 bis 6 Kohlenstoffatomen sind.

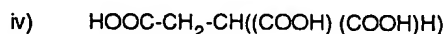
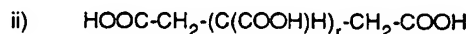
20. Zusammensetzung nach Anspruch 19, in welcher A ein gesättigter aliphatischer Rest mit 2,3 oder 4 Kohlenstoffatomen, m eine ganze Zahl von 0 bis 4, n 0, 1, oder 2 und die Summe m + n 2 bis 4 ist, und R und R₁, unabhängig voneinander, Alkylreste mit 1, 2, 3 oder 4 Kohlenstoffatomen sind.

21. Zusammensetzung nach irgendeinem der vorhergehenden Ansprüche 1 bis 18, in welcher der Weichmacher ein Esterderivat von mindestens einem der folgenden Bestandteile ist:



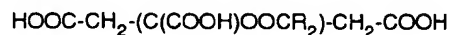
worin q und r, unabhängig voneinander, 1, 2, 3 oder 4 sind, und R₂ ein Methyl- oder Propylrest ist.

22. Zusammensetzung nach dem vorhergehenden Anspruch, in welcher der Weichmacher ein Methyl-, Ethyl-, Propyl- oder Butylcarboxylatester eines Bestandteils, ausgewählt aus der aus



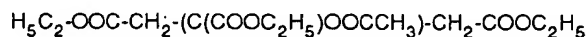
bestehenden Gruppe, ist, wobei R_2 ein Methyl- oder Propylrest ist.

23. Zusammensetzung nach dem vorhergehenden Anspruch, in welcher der Weichmacher ein Triethyl- oder Tributyl-carboxylatester von

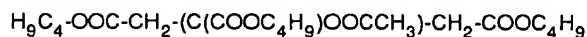


ist,
wobei R_2 ein Methyl- oder Propylrest ist.

24. Zusammensetzung nach dem vorhergehenden Anspruch, in welcher der Weichmacher aus der aus



und



bestehenden Gruppe ausgewählt ist.

25. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 18, in welcher der Weichmacher ein Mono-, Di- oder Triester von



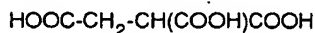
ist.

26. Zusammensetzung nach Anspruch 25, in welcher der Weichmacher das Triacetat von Glycerol, nämlich



ist.

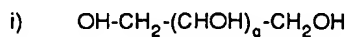
27. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 18, in welcher der Weichmacher ein Diacetatmonopropionat oder Dipropionatmonoacetat von Glycerin oder das Diacetat oder Dipropionat von $\text{OH-CH}_2\text{-C(COOH)H-CH}_2\text{OH}$ oder der Trimethylester oder Tripropylester von

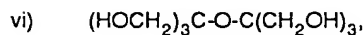
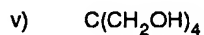
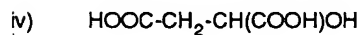
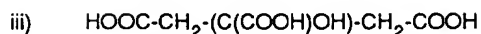
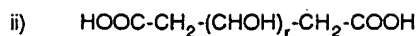


ist.

28. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 18, in welcher A ein gesättigter aliphatischer Rest mit 2, 3 oder 4 Kohlenstoffatomen, x 1 oder 2, y eine ganze Zahl von 0 bis 4, z eine ganze Zahl von 0 bis 4 und die Summe $y + z$ 2 bis 4 ist, und R und R_1 , unabhängig voneinander, Alkylreste mit 1, 2, 3 oder 4 Kohlenstoffatomen sind.

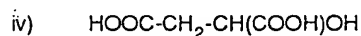
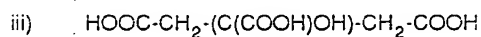
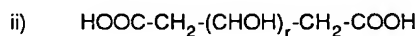
29. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 18, in welcher der Weichmacher ein Esterderivat von mindestens einem der folgenden Bestandteile ist:





worin q und r, unabhängig voneinander, 1, 2, 3 oder 4 sind.

30. Zusammensetzung nach dem vorhergehenden Anspruch, worin der Weichmacher ein Methyl-, Ethyl-, Propyl- oder Butylcarboxylatester eines Bestandteils, ausgewählt aus der aus



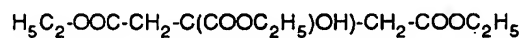
bestehenden Gruppe, ist.

31. Zusammensetzung nach dem vorhergehenden Anspruch, worin der Weichmacher ein Triethyl- oder Tributylcarboxylatester von



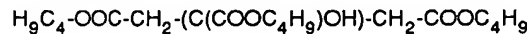
ist.

32. Zusammensetzung nach Anspruch 31, worin der Weichmacher die Formel



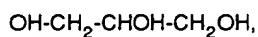
aufweist.

33. Zusammensetzung nach Anspruch 23, worin der Weichmacher die Formel

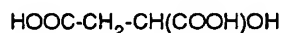


aufweist.

34. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 18, in welcher der Weichmacher das Diacetat oder Dipropionat von



oder der Monoacetatdimethylester oder Monoacetatdipropylester oder Monopropionatdipropylester von



ist.

35. Zusammensetzung nach Anspruch 18, worin der Weichmacher aus der aus Triacetylcitrat, Triethylacetylcitrat, Triethylenglycol-di(2-ethylbutyrat), Diacetin, acetylierten Monoglyceriden, Triethylcitrat, Diethylsuccinat, Dimethylsebacat, Di-n-hexylazelat, Diisooctylazelat, Di-(2-ethylhexyl)azelat, Dicapryladipat und Mischungen daraus bestehenden Gruppe ausgewählt ist.

36. Zusammensetzung nach Anspruch 35, in welcher der Weichmacher Dimethylsebacat, Diethylsuccinat, Acetyltriethylcitrat oder Mischungen daraus ist.

37. Zusammensetzung nach entweder den Ansprüchen 34, 35 oder 36, in welcher der thermische Stabilisator und das Formtrennmittel in der Zusammensetzung in Mengen von etwa 0,01 bis etwa 5 % und von etwa 0,01 bis etwa 2 Gew.-%, bezogen auf den Stärkeesterbestandteil der Zusammensetzung, vorliegen.

38. Zusammensetzung nach irgendeinem vorhergehenden Anspruch, die darüber hinaus eine native oder chemisch modifizierte (nicht veresterte) Stärke, ausgewählt aus Kartoffeln, Reis, Tapioca, Mais, Erbsen, Roggen, Hafer und Weizen, ist.

39. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 38, geformt als Artikel.

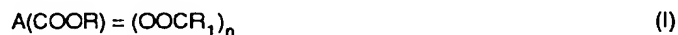
40. Artikel nach Anspruch 39, ausgewählt aus der aus Flaschen, Strängen, Blättern, Filmen, Verpackungsmaterialien, Rohren, Tassen, Stäben, laminierten Filmen, Säcken, Taschen, pharmazeutischen Kapseln, Schäumen, Granulaten und Pudern bestehenden Gruppe.

41. Verfahren zur Herstellung der Artikel nach Anspruch 40, ausgewählt aus der aus Spritzgießen, Kompressionsgießen, Filmverarbeiten, Blasgießen, Vakuumformen, Warmformen, Extrudieren, Extrusionsgießen, Coextrudieren, Schäumen, Profilextrudieren und Kombinationen daraus bestehenden Gruppe.

42. Schmelze, aus der die Zusammensetzung nach irgendeinem der Ansprüche 1 bis 41 erhalten wird.

Revendications

1. Composition obtenue à partir d'une masse fondue comprenant de l'amidon estérifié, un plastifiant et si on le désire d'autres additifs, caractérisée en ce que l'amidon estérifié a un degré de substitution de 1,8 à 2,9, l'amidon estérifié comprenant au moins deux membres choisis dans le groupe constitué de l'acétate, du propionate, du butyrate, du pentanoate, de l'hexanoate, de l'heptanoate et de l'octanoate, à l'exception d'esters d'amidon ayant à la fois un radical acétate et un radical acide carboxylique en C₆, et dans laquelle le plastifiant répond à la formule



dans laquelle A est un radical aliphatique ou alicyclique saturé ou insaturé ; n est un entier ; m est un entier de 0 à 6, tel que la somme m + n soit un entier de 1 à 6, et R et R₁ sont, indépendamment l'un de l'autre, un radical aliphatique ou alicyclique saturé ou insaturé en C₁ à C₂₀, ou



dans laquelle A est un radical aliphatique ou alicyclique saturé ou insaturé ; x est un entier de 1 à 2 ; y est un entier de 0 à 4 ; z est un entier de 0 à 4 ; la somme y + z étant un entier de 2 à 4 et R et R₁ sont, indépendamment l'un de l'autre, un radical aliphatique ou alicyclique saturé ou insaturé en C₁ à C₆.

ou est choisi dans le groupe constitué du phtalate de diméthyle, du phtalate de diéthyle, du phtalate de dibutyle, du phtalate de dihexyle, du phtalate de di-2-éthylhexyle, du phtalate de di-n-octyle, du phtalate de diisooctyle, du phtalate de di-isononyl, du phtalate de diisodécyle, du phtalate de dicyclohexyle, du phtalate de diméthylcyclohexyle, du phtalate de diméthylglycol, du phosphate de trichloréthyle, du phosphate de crésyle-diphényle, du phosphate de triphényle, du phosphate de tricrésyle, du glycolate de butylphtalylbutyle, du phosphate de tributyle, du N-éthyl-o,p-toluènesulfonamide, du dibenzoate de diéthylèneglycol, du dibenzoate de dipropylèneglycol et de mélanges de ceux-ci.

2. Composition selon la revendication 1, dans laquelle l'amidon estérifié comprend au moins deux membres choisis dans le groupe constitué des acétates, des propionates, des butyrates, des pentanoates et des hexanoates.

3. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'ester d'amidon a été obtenu par réaction de l'amidon avec un anhydride d'acide mixte ou avec un mélange d'anhydrides d'acides différents.

4. Composition selon la revendication 2, dans laquelle l'ester d'amidon comprend à la fois des groupes acétate et propionate liés à une molécule d'amidon commune.

5. Composition selon la revendication 2, dans laquelle l'amidon comprend à la fois des groupes acétate et butyrate liés à une molécule d'amidon commune.

6. Composition selon la revendication 2, dans laquelle l'amidon comprend à la fois des groupes propionate et butyrate liés à une molécule d'amidon commune.

7. Composition selon la revendication 2, dans laquelle l'amidon comprend à la fois des groupes pentanoate et butyrate liés à une molécule d'amidon commune.

8. Composition selon l'une quelconque des revendications précédentes, dans laquelle le rapport des membres est d'environ 20:1 à 1:20.

9. Composition selon la revendication 8, dans laquelle le rapport des membres est d'environ 3,1 à 1,3.

10. Composition selon la revendication 9, dans laquelle le rapport des membres est d'environ 2:1 à 1:2.

11. Composition selon la revendication 10, dans laquelle le rapport des membres est d'environ 1:1.

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle le degré de substitution est de 1,8 à environ 2,5.

13. Composition selon l'une quelconque des revendications précédentes, dans laquelle la teneur en amylose est d'au moins environ 50 % en poids par rapport à l'amidon.

14. Composition selon l'une quelconque des revendications précédentes, dans laquelle la teneur en amylose est d'au moins environ 70 % en poids par rapport à celle de l'amidon.

15. Composition selon l'une quelconque des revendications précédentes, dans laquelle la teneur en amylose est d'au moins environ 80 % en poids par rapport à celle de l'amidon.

16. Composition selon l'une quelconque des revendications précédentes, dans laquelle la teneur en amylose est d'au moins environ 90 % en poids par rapport à celle de l'amidon.

17. Composition selon l'une quelconque des revendications précédentes, qui comprend en outre un membre choisi dans le groupe constitué des plastifiants secondaires ; des charges ; de matières provenant du bois ; des oxydes de magnésium, d'aluminium, de silicium et de titane ; des lubrifiants, des agents de démoulage ; des plastifiants ; des stabilisants ; des agents colorants ; des retardateurs de combustion ; des composés du bore ; des sels de métaux alcalins ou alcalino-terreux ; des stabilisants thermiques ; et des accélérateurs d'écoulement à l'état fondu ; et des mélanges de ceux-ci.

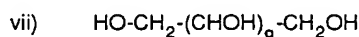
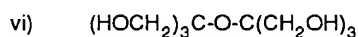
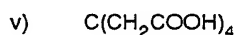
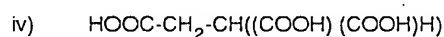
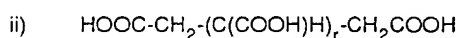
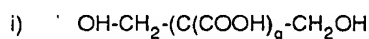
18. Composition selon l'une quelconque des revendications précédentes, dans laquelle un plastifiant est présent dans

une proportion de 5 à 60 % en poids par rapport à celle de l'ester d'amidon.

19. Composition selon l'une quelconque des revendications précédentes, dans laquelle A est un radical aliphatique saturé en C₂ à C₈; m est un entier de 0 à 4; n est 0, 1, 2 ou 3; la somme m + n est égale à 2 ou 4; et R et R₁ sont indépendants l'un de l'autre et sont des radicaux alcoyle en C₁ à C₆.

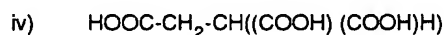
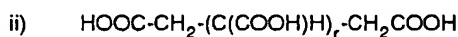
20. Composition selon la revendication 19, dans laquelle A est un radical aliphatique saturé ayant 2, 3 ou 4 atomes de carbone; m est un entier de 0 à 4; n est 0, 1 ou 2; la somme m + n est égale à 2 à 4; et R et R₁ sont indépendants l'un de l'autre et sont des radicaux alcoyle ayant 1, 2, 3 ou 4 atomes de carbone.

21. Composition selon l'une quelconque des revendications 1 à 18, dans laquelle le plastifiant est un ester d'au moins un des membres suivants :



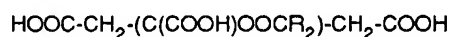
dans lesquels q et r sont, indépendamment l'un de l'autre, 1, 2, 3 ou 4 et R₂ est un radical méthyle ou propyle.

22. Composition selon la revendication précédente, dans laquelle le plastifiant est un ester carboxylique de méthyle, d'éthyle, de propyle ou de butyle d'un membre choisi dans le groupe constitué de :



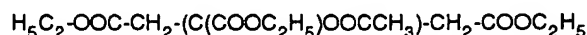
dans lesquels R₂ est un groupe méthyle ou propyle.

23. Composition selon la revendication précédente, dans laquelle le plastifiant est un ester carboxylique de triéthyle ou de tributyle de :

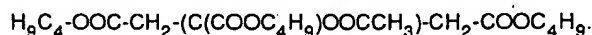


où R₂ est un groupe méthyle ou propyle.

24. Composition selon la revendication précédente, dans laquelle le plastifiant est choisi dans le groupe constitué de



et de



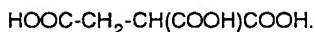
25. Composition selon l'une quelconque des revendications 1 à 18, dans laquelle le plastifiant est un mono, di ou triester de



26. Composition selon la revendication 25, dans laquelle le plastifiant est le triacétate de glycérol, c'est-à-dire :

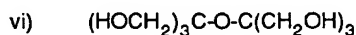
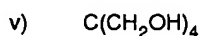
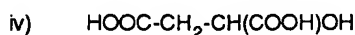
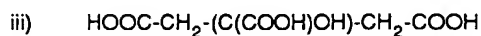
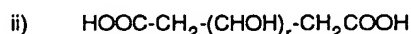
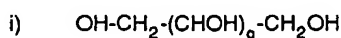


27. Composition selon l'une quelconque des revendications 1 à 18, dans laquelle le plastifiant est un diacétate-monopropionate ou un dipropionate-monoacétate de glycérol, ou bien le diacétate ou le dipropionate de $\text{OH-CH}_2\text{-C(COOH)H-CH}_2\text{OH}$, ou bien l'ester triméthylrique ou l'ester tripropylique de



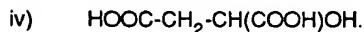
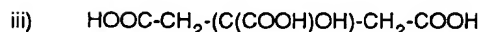
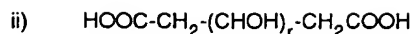
28. Composition selon l'une quelconque des revendications 1 à 18, dans laquelle A est un radical aliphatique saturé en C_2 , C_3 ou C_4 ; x est 1 ou 2 ; y est un entier de 0 à 4 ; z est un entier de 0 à 4 ; la somme y + z est de 2 à 4 ; et R et R_1 sont indépendants l'un de l'autre et sont des radicaux alcoyle en C_1 , C_2 , C_3 ou C_4 .

29. Composition selon l'une quelconque des revendications 1 à 18, dans laquelle le plastifiant est un ester d'au moins un des membres suivants :



dans lesquels q et r sont, indépendamment l'un de l'autre, 1, 2, 3 ou 4.

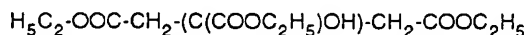
30. Composition selon la revendication précédente, dans laquelle le plastifiant est un ester carboxylique de méthyle, d'éthyle, de propyle ou de butyle d'un membre choisi dans le groupe constitué de :



31. Composition selon la revendication précédente, dans laquelle le plastifiant est un ester carboxylique de triéthyle ou de tributyle de :



32. Composition selon la revendication 31, dans laquelle le plastifiant répond à la formule :



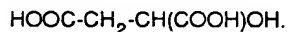
33. Composition selon la revendication 23, dans laquelle le plastifiant répond à la formule :



34. Composition selon l'une quelconque des revendications 1 à 18, dans laquelle le plastifiant est le diacétate ou le dipropionate de :



ou le monoacétate-ester diméthylque ou le monoacétate-ester dipropylique ou le mono-propionate-ester dipropylique de :



35. Composition selon la revendication 18, dans laquelle le plastifiant est choisi dans le groupe constitué du citrate de triacétyle, du citrate de triéthyle-acétyle, du triéthylèneglycol di (2-butyrate d'éthyle), de la diacétine, des monoglycérides acétylés, du citrate de triéthyle, du succinate de diéthyle, du sébacate de diméthyle, de l'azélate de di-n-hexyle, de l'azélate de di-isooctyle, de l'azélate de di-(2-éthylhexyle), de l'adipate de dicapryle et de mélanges de ceux-ci.

36. Composition selon la revendication 35, dans laquelle le plastifiant est le sébacate de diméthyle, le succinate de diéthyle, le citrate d'acétyltriéthyle ou des mélanges de ceux-ci.

37. Composition selon l'une quelconque des revendications 34, 35 ou 36, dans laquelle le stabilisant thermique et l'agent de démoulage sont présents dans la composition dans des proportions qui sont respectivement d'environ 0,01 à environ 5 % et d'environ 0,01 à environ 2 % en poids par rapport au constituant ester d'amidon de la composition.

38. Composition selon l'une quelconque des revendications précédentes, comprenant en outre un amidon naturel ou chimiquement modifié (non estérifié) choisi parmi les amidons de pomme de terre, de riz, de manioc, de seigle, de pois, d'avoine, de froment et de blé.

39. Composition selon l'une quelconque des revendications 1 à 38, lorsqu'elle est transformée en articles.

40. Articles selon la revendication 39, choisis dans le groupe constitué de bouteilles, de joncs, de feuilles, de films,

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de matériaux d'emballage, de tuyaux, de gobelets, de baguettes, de films stratifiés, de sacs, de sachets, de capsules pharmaceutiques, de moules, de granulés et de poudrés.

5 41. Procédé de fabrication des articles selon la revendication 40, choisi dans le groupe constitué du moulage par injection, du moulage par compression, de la transformation en film, du moulage par soufflage, du formage sous vide, du thermoformage, de l'extrusion, du moulage par extrusion, de la coextrusion, du moussage, de l'extrusion de profilés et de combinaisons de ceux-ci.

10 42. Masse fondue à partir de laquelle est obtenue la composition selon l'une quelconque des revendications 1 à 41.

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